Ab initio Molecular Dynamics Study of Dependence of von Weizsäcker Kinetic Energy Term on Atomic Disorder

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Ⅰ. Introduction

The density functional theory(DFT) by Hohenberg and Kohn(HK)[1] has brought about a great progress in material science from a theoretical point of view. They have proved that the total energy of a system can be expressed in a functional of the electron charge density. Starting from the HK theory, Kohn and Sham(KS)[2] have derived an expression for the total energy of the system. In the KS theory, the kinetic energy of the electrons is calculated by solving one-particle Schrödinger equation which is called *KS equation*. Incorporating the many particle interaction terms into the exchange-correlation potential and energy, they have represented the kinetic energy as that of non-interacting particles. They also used the local density approximation, which is the theory for the *inhomogeneous* electron gas. In the theory, the exchange-correlation potential and energy are locally approximated by that of *homogeneous* electron gas, and they are expressed only in the functional of electron charge density.

The spirit of the DFT by Hohenberg and Kohn is to express the ground state energy in terms of the charge density without using wave functions. Such DFT is called *orbital-free DFT*. The spirit comes from an earlier density functional proposed by Thomas[3] and Fermi[4](TF), which expresses an exact energy for the system of the non-interacting *homogeneous* electron gas. The functional is called *TF energy functional*. In the KS theory, a long computational time has been required depending on the number of orbitals. However, if we can evaluate the kinetic energy without solving the KS equation, we can obtain the total energies in a short computational time. On the other hand, although the TF energy functional is valid for slowly varying densities, it is insufficient as for rapidly varying densities. So, von Weizsäcker[5] proposed a correction term for the TF energy functional. It is called *von Weizsäcker energy functional*. The energy

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[1] Hohenberg, P. and Kohn, W., "Inhomogeneous Electron Gas", *Phys.Rev.* vol.136, 1964, pp.864～871.

[2] Kohn, W. and Sham, L.J. "Self-Consistent Equations Including Exchange and Correlation Effects", *Phys.Rev.*A vol.140, 1965, pp.1133～1138.

[3] Thomas, L.H., "The calculation of atomic fields" *Proc. Cambridge Phil. Soc.* vol.23, 1927, pp.542～548.

[4] Fermi, E., "Un Metodo Statistico per la Determinazione di alcune Prioprieta dell'Atomo" *Rend. Accad. Naz. Lincei*, vol.6, 1927, pp.602～607.

[5] von Weizsäcker, C.F., "Zur Theorie der Kernmassen", *Z.Phys.* vol.96, 1935, pp.431～458.

functional is nine times greater than the second-order term of the density gradient expansion.[6] The TF energy functional combined with the von Weizsäcker energy functional is called *Thomas-Fermi-von Weizsäcker(TFvW) energy functional*. Jones and Young[7] have shown that the TF energy functional gives a correct second-order kinetic energy for the slowly varying density limit and the von Weizsäcker energy functional gives the correct one for the rapidly varying density limit.

The earlier studies[8] on the calculation of the orbital-free density functional(OFDF) have been non-self-consistent in which the charge densities have been obtained by Hartree-Fock(HF) or KS calculation. The OFDF method proposed by Pearson et al.[9] succeeded in the self-consistent calculation using an *ab initio* molecular dynamics(AIMD) method, in which they used a Perrot functional[10] as the kinetic energy functional. The Perrot functional, which is based on the linear response theory, is a modified form of the TFvW energy functional. They calculated the lattice parameter, bulk modulus, vacancy formation energy, and phonon dispersion curve in the crystalline sodium system.[11] Their results were in agreement with the experiments.

The AIMD technique developed by Car and Parrinello(CP)[12] is one of the powerful tools to explore both the dynamical and statistical properties of the condensed systems. In the method, the coupled equations for ions and electrons are solved so as to nearly trace the bottom of the Born-Oppenheimer potential surface. In the past 25 years, many efforts have been focusing on reducing computational time of the AIMD method. For instance, they are modifications of the pseudopotentials,[13] improvements of the algorithms to optimize the electronic system such as the conjugate gradient method,[14] and the order-*N* methods.[15] The last method makes it

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6) Dreizler, R.M. and Gross, E.K.U., *Density Functional Theory*, Springer-Verlag, Berlin, 1990.

7) Jones, W., “Density functionals for conduction electrons in metals”, *Phys.Lett.A* vol.34, 1971, pp.351～352; Jones, W. and Young, W.H., “Density functional theory and the von Weizsäcker method”, *J.Phys.C: Solid State Phys.* vol.4, 1971, pp.1332～1330.

8) Jones, R.O. and Gunnarsson, O., “The density functional formalism, its applications and prospects”, *Rev. Mod.Phys*. vol.61, 1989, pp.689～746.

9) Pearson, M., Smargiassi, E., and Madden, P.A., “*Ab initio* molecular dynamics with an orbital-free density functional”, *J.Phys.Condens. Matter* vol.5, 1993, pp.3221～3240.

10) Perrot, F., “Hydrogen-hydrogen interaction in an electron gas”, *J.Phys. Condens. Matter* vol.6, 1993, pp.431～446.

11) Smargiassi, E., and Madden, P.A., “Free energies of point degects in sodium from first-principles molecular-dynamics simulations”, *Phys.Rev.*B vol.51, 1995, pp.129～136; Smargiassi, E. and Madden, P.A., “Free-energy calculations in solids from first-principles molecular dynamics：Vacancy formation in sodium”, *Phys.Rev.*B vol.51, 1995, pp.117～128.

12) Car, R. and Parrinello, M., “Unified approach for molecular dynamics and density-functional theory”, *Phys.Rev.Lett.* vol.55, 1985, pp.2471～2474.

13) Vanderbilt, D., “Soft self-consistent pseudopotentials in a generalized eigenvalue formalism”, *Phys.Rev.*B vol.41, 1990, pp.7892-7895; Troullier, N. and Martins, J.L., “Efficient pseudopotentials for plane-wave calculations”, *Phys.Rev.*B vol.43, 1991, pp.1993～2006.

14) Štich, I., Car, R., Parrinello, M., and Baroni, S., “Conjugate gradient minimization of the energy functional: A new method for electronic structure calculation”, *Phys.Rev.*B vol.39, 1989, pp. 4997～5004; Teter, M.P., Payne, M.C., and Allan, D.C., “Solution of Schrodinger’s equation for large systems”, *Phys.Rev.*B vol.40, 1989, pp.12255～12263; Gillan, M.J., “Calculation of the vacancy formation energy in aluminium”,

possible to treat the large systems such as disordered systems, layered structures, large clusters, and so on. The AIMD method with the OFDF is one of the order-*N* methods and has been applied to the large systems such as the local elasticity analysis in sodium glasses,[16] the static and dynamic structure factors in sodium liquids,[17] and the geometrical analysis of the simple metal clusters[18] and surfaces.[19]

Jones and Young have shown by use of perturbation theory that the von Weizsäcker energy is effective for describing the electronic structure in a rapidly varying potential. However, there has been no study on the dependence of the von Weizsäcker energy on atomic disorder which occurs at elevated temperature in a realistic system. In the present paper, we compare the temperature dependence of the TF and von Weizsäcker energies in the sodium system by use of the AIMD method with the OFDF, and analyze their energy spectra.

This paper is organized as follows. The next Chapter Ⅱ describes several orbital-free kinetic energy functionals. Chapter Ⅲ describes AIMD method with an OFDF. In Chapter Ⅳ, the computational details are presented. In Chapter Ⅴ, we perform numerical studies, and discuss on the results. Summary and conclusions are in Chapter Ⅵ. Appendix describes the theory of *homogeneous* electron gas.

Atomic (Hartree) units will be used throughout the paper, unless otherwise stated.

Ⅱ. Orbital-Free Kinetic Energy Functionals

1. Thomas-Fermi kinetic energy functional

The spirit of the DFT by Hohenberg and Kohn[20] is to express the ground state energy only in charge density. The first explicitly formulated kinetic energy functional is the TF functional, proposed independently by Thomas[21] and Fermi,[22] with the form

$$T_{TF}[\rho] = C_{TF}\int_{cell}\rho(\vec{r})^{\frac{5}{3}}d\vec{r}, \qquad C_{TF} = \frac{3}{10}\left(3\pi^2\right)^{\frac{2}{3}}, \tag{1}$$

which is a local approximation based on the theory of the non-interacting *homogeneous*

J.Phys.Condens.Matter vol.1, 1989, pp. 689～712.

15) Galli, G. and Parrinello, M., "Large scale electronic structure calculations", *Phys.Rev.Lett.* vol.69, 1992, pp.3547～3550; Baroni, S. and Giannozzi, P., "Towards Very Large-Scale Electronic-Structure Calculations", *Europhys.Lett.* vol.17, 1992, pp.547～552; Li, X.P., Nunes, W., and Vanderbilt, D., "Density-matrix electronic-structure method with linear system-size scaling", *Phys.Rev.*B vol.47, 1993, pp.10891～10894.

16) Aoki, M.I. and Tsumuraya, K., "*Ab initio* molecular dynamics studies on volume stability of Voronoi polyhedra under pressures in a metal glass", *J.Chem.Phys*. vol.104, 1996, pp. 6719～6723.

17) Foley, M., Smargiassi, E., and Madden, P.A., "The dynamic structure of liquid sodium from *ab initio* simulation", *J.Phys.Condens.Matter* vol.6, 1994, pp.5231～5241.

18) Shah, V., Nehete, D., and Kanhere, D.G., "*Ab initio* molecular dynamics via density based energy functionals", *J.Phys.Condens.Matter* vol.6, 1994, pp.10773～10781; Nehete, D., Shah, V., and Kanhere, D.G., "AIMD using density-based energy functionals: Application to ground-state geometries of some small clusters", *Phys.Rev.*B vol.53, 1996, pp.2126～2131.

19) Govind, N., Wang, J., and Guo, H., "Total-energy calculations using a gradient-expanded kinetic-energy functional", *Phys.Rev.*B vol.50, 1994, pp. 11175～11178.

20) Hohenberg, P. and Kohn, W., "Inhomogeneous Electron Gas", *Phys.Rev.* vol.136, 1964, pp.864～871.

21) Thomas, L.H., "The calculation of atomic fields" *Proc. Cambridge Phil. Soc.* vol.23, 1927, pp.542～548.

22) Fermi, E., "Un Metodo Statistico per la Determinazione di alcune Prioprieta dell'Atomo" *Rend. Accad. Naz.*

electron gas (see Appendix). The functional has been found to be exact for the atoms in the limits of the infinite atomic number and the high electron density. However, the functional has serious defects, when the functional is applied to the realistic systems. For instance, the functional gives the charge density to be infinite at the nucleus of an atom and to decay as r^{-6} far from the nucleus.[23] Thus the density does not decay exponentially. Another serious defect of the functional is the lack of shell structure of atom. In addition, the functional leads no atomic binding to form molecules or solids.[24] It is called *non-binding theorem*.

2. von Weizsäcker functional

von Weizsäcker[25] has taken into account the effect of the *inhomogeneity* of the electron density for the TF kinetic energy functional by adding the correction term given by

$$T_{vW}[\rho] = \frac{1}{8}\int_{cell} \frac{|\nabla\rho(\vec{r})|^2}{\rho(\vec{r})} d\vec{r}\,, \tag{2}$$

which is called *von Weizsäcker energy functional*. The functional gives an asymptotic behavior of the exact kinetic energy functional for a rapidly varying perturbation.[26] The TF functional combined with the von Weizsäcker energy functional is called *TFvW kinetic energy functional* given by

$$T_{TFvW}[\rho] = T_{TF}[\rho] + T_{vW}[\rho]\,. \tag{3}$$

A modified TFvW functional is given by

$$T_{TFvW-\lambda}[\rho] = T_{TF}[\rho] + \lambda T_{vW}[\rho]\,, \tag{4}$$

where λ is an empirical parameter of which the value is between 1/9 and 1. This is called *TFvW-λ kinetic energy functional*. These functionals improve the behavior of the densities near the nucleus and asymptotically far from the nucleus.[27] Furthermore, they improve the binding states between the atoms to form molecules.[28] However, the functionals don't result in the Friedel oscillation which is an essential feature in metallic systems.

3. Density gradient expansion

For slowly varying perturbations, the density gradient expansion of the kinetic energy[29] is represented by

$$T[\rho] = T^{(0)}[\rho] + T^{(2)}[\rho] + T^{(4)}[\rho] + \ldots\,. \tag{5}$$

Each term in Eq.(5) can be expressed by

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[23] Dreizler, R.M. and Gross, E.K.U., *Density Functional Theory*, Springer-Verlag, Berlin, 1990.

[24] Jones, R.O. and Gunnarsson, O., "The density functional formalism, its applications and prospects", *Rev. Mod.Phys*. vol.61, 1989, pp. 689～746.

[25] von Weizsäcker, C.F., "Zur Theorie der Kernmassen", *Z.Phys.* vol.96, 1935, pp.431～458.

[26] Jones, W., "Density functionals for conduction electrons in metals", *Phys.Lett.A* vol.34, 1971, pp.351～352; Jones, W. and Young, W.H., "Density functional theory and the von Weizsäcker method", *J.Phys.C: Solid State Phys.* vol.4, 1971, pp. 1332～1330.

[27] Jones, R.O. and Gunnarsson, O., "The density functional formalism, its applications and prospects", *Rev. Mod.Phys*. vol.61, 1989, pp. 689～746.

[28] Yonei, K., "An Extended Thomas-Fermi-Dirac Theory for Diatomic Molecule", *J.Phys.Soc.Jpn.* vol.31, 1971, pp.882～894.

[29] Dreizler, R.M. and Gross, E.K.U., *Density Functional Theory*, Springer-Verlag, Berlin, 1990.

$$T^{(2\ell)}[\rho] = \int d\vec{r}\, t^{(2\ell)}(\vec{r}), \tag{6}$$

where

$$t^{(0)}(\vec{r}) = C_0 \rho(\vec{r})^{\frac{5}{3}}, \qquad C_0 = \frac{3}{10}\left(3\pi^2\right)^{\frac{2}{3}}, \tag{7}$$

$$t^{(2)}(\vec{r}) = C_2 \frac{[\nabla\rho(\vec{r})]^2}{\rho(\vec{r})}, \qquad C_2 = \frac{1}{72}, \tag{8}$$

and

$$t^{(4)}(\vec{r}) = C_4 \rho(\vec{r})^{\frac{1}{3}} \left[\left\{ \frac{\Delta\rho(\vec{r})}{\rho(\vec{r})} \right\}^2 - \frac{9}{8} \left\{ \frac{\Delta\rho(\vec{r})}{\rho(\vec{r})} \right\} \left\{ \frac{\nabla\rho(\vec{r})}{\rho(\vec{r})} \right\}^2 + \frac{1}{3} \left\{ \frac{\nabla\rho(\vec{r})}{\rho(\vec{r})} \right\}^4 \right],$$

$$C_4 = \frac{1}{540\left(3\pi^2\right)^{2/3}}. \tag{9}$$

The zero-th order kinetic energy term $T^{(0)}[\rho]$ corresponds to the TF functional, and the second-order kinetic energy term $T^{(2)}[\rho]$ differs from the von Weizsäcker energy functional by a factor 1/9, i.e., this corresponds to λ=1/9 in Eq.(4). Thus the TFvW-λ kinetic energy with λ=1/9 is a sufficient approximation for the slowly varying perturbations.

4. Linear-response theory

For the small perturbations, the correct form has been given by the linear-response theory.[30] In the theory, if the electron charge density induced by a external potential is defined as

$$\rho(\vec{r}) \equiv \bar{\rho} + \delta\rho(\vec{r}), \tag{10}$$

where $\bar{\rho}$ is the average electron density and $|\delta\rho| << 1$, then the kinetic energy is given by

$$T_{TF}[\rho] = T_{TF}[\bar{\rho}] + \frac{1}{2}\iint d\vec{r}\, d\vec{r}\,' K_{TF}(\vec{r},\vec{r}\,')\delta\rho(\vec{r})\delta\rho(\vec{r}\,'), \tag{11}$$

where the kernel $K_{TF}(\vec{r},\vec{r}\,')$ is defined as

$$K_{TF}(\vec{r},\vec{r}\,') \equiv \frac{\delta^2 T_{TF}[\rho]}{\delta\rho(\vec{r})\delta\rho(\vec{r}\,')}. \tag{12}$$

Fourier space representation of Eq.(11) is given by

$$T_{TF}[\rho] = T_{TF}[\bar{\rho}] + \frac{1}{2(2\pi)^3}\int d\vec{G} K_{TF}(\vec{G})\rho_G^* \rho_G$$

$$= T_{TF}[\bar{\rho}] + \frac{\Omega}{2}\sum_G \rho_G^* \rho_G K_{TF}(\vec{G}), \tag{13}$$

with

$$K_{TF}(\vec{G}) = -\frac{1}{\chi_{TF}}, \qquad \chi_{TF} = -\frac{k_F}{\pi^2}, \qquad k_F = \left(3\pi^2\bar{\rho}\right)^{1/3}, \tag{14}$$

where Ω is the volume of supercell, $K_{TF}(\vec{G})$ is Fourier coefficient of $K_{TF}(\vec{r})$, χ_{TF} is the

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[30] Jones, R.O. and Gunnarsson, O., "The density functional formalism, its applications and prospects", *Rev. Mod.Phys*. vol.61, 1989, pp. 689～746.

screened response function or the screened susceptibility, and k_F is the Fermi wave vector.

Hohenberg and Kohn[31] used the Lindhard function χ_0 instead of the χ_{TF}, i.e.,

$$T_{HK}[\rho] = T_{TF}[\overline{\rho}] + \frac{\Omega}{2}\sum_G \rho_G^* \rho_G K_0(\vec{G}), \tag{15}$$

with

$$K_0(\vec{G}) = -\frac{1}{\chi_0}, \qquad \chi_0 = -\frac{k_F}{\pi^2}\left(\frac{1}{2} + \frac{1-\eta^2}{4\eta} ln\left|\frac{1+\eta}{1-\eta}\right|\right), \tag{16}$$

where $\eta = G/2k_F$ and the T_{HK} is the HK kinetic energy functional. The function χ_0 is an exact response function. It is known that $\chi_0 \to \chi_{TF}$ in the limit of low *G*. The HK kinetic energy functional is found to result in the Friedel oscillation.[32] However, the functional leads to *negative density problem* in the limit of large *G*.

Jones and Young[33] have proposed a response function $\chi_{TFvW-\lambda}(G)$ for the TFvW-λ kinetic energy functional in Eq.(4) given by

$$\chi_{TFvW-\lambda}(G) = -\frac{k_F}{\pi^2}\frac{1}{1+3\lambda\eta^2}\,. \tag{17}$$

Figure 1 shows the response functions as a function of *G*. The functions $\chi_{TFvW-\lambda}(G)$ with λ=1/9 is corresponded to the correct linear response functions in the limits of low *G*, and the $\chi_{TFvW-\lambda}(G)$ with λ=1 is corresponded to the correct linear response functions in the limits of large *G*. The linearized form of the TFvW kinetic energy functional is expressed as

$$T_{lin}[\rho] = T_{TFvW}[\overline{\rho}] + \frac{\Omega}{2}\sum_G \rho_G^* \rho_G K_{TFvW}(\vec{G}), \tag{18}$$

with

$$K_{TFvW}(\vec{G}) = -\frac{1}{\chi_{TFvW}(\vec{G})}\,. \tag{19}$$

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[31] Hohenberg, P. and Kohn, W., “Inhomogeneous Electron Gas”, *Phys.Rev.* vol.136, 1964, pp.864～871.

[32] Pearson, M., Smargiassi, E., and Madden, P.A., “*Ab initio* molecular dynamics with an orbital-free density functional”, *J.Phys.Condens. Matter* vol.5, 1993, pp.3221～3240.

[33] Jones, W., “Density functionals for conduction electrons in metals”, *Phys.Lett.A* vol.34, 1971, pp.351～352; Jones, W. and Young, W.H., “Density functional theory and the von Weizsäcker method”, *J.Phys.C: Solid State Phys.* vol.4, 1971, pp. 1332～1330.

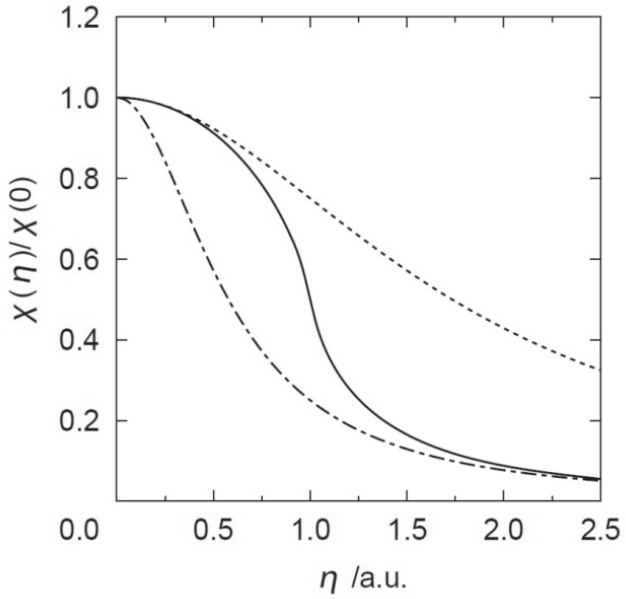

Fig.1. Response functions as a function of η. The solid line is Lindhard function χ_0, the dotted line is the response function $\chi_{TFvW-\lambda}(G)$ with λ=1/9, and the dash-dotted line is the $\chi_{TFvW-\lambda}(G)$ with λ=1.

5. Perrot functional

Perrot[34)] has proposed an excellent electron kinetic energy functional $T_P[\rho]$, *Perrot functional*, incorporating both attractive properties of the TFvW and HK functionals. The functional is given by

$$T_P[\rho(\vec{r})] = T_{TFvW}[\rho(\vec{r})] + \frac{\Omega}{2}\sum_G \rho_G^* \rho_G K_P(G), \tag{20}$$

where

$$K_P(G) = -\left(\frac{1}{\chi_0} - \frac{1}{\chi_{TFvW}}\right). \tag{21}$$

The functional is also expressed by

$$T_P[\rho] = T_{TFvW}[\rho] - T_{lin}[\rho] + T_{HK}[\rho]. \tag{22}$$

This functional is found to give a correct linear response for all *G* since $T_{TFvW} = T_{lin}$ for small perturbation. In addition, it is asymptotically exact in the limit of large *G* (since as $G \to \infty$, $T_{lin} = T_{HK}$) for perturbations with all sizes. Therefore, this prevents the negative density problem encountered in the functional T_{HK} and also results in the Friedel oscillation.

[34)] Perrot, F., "Hydrogen-hydrogen interaction in an electron gas", *J.Phys. Condens. Matter* vol.6, 1993, pp.431～446.

Ⅲ. *Ab initio* Molecular Dynamics Method with an Orbital-Free Density Functional

The AIMD method with the OFDF developed by Pearson et al.[35] uses the Perrot functional as the kinetic energy functional which is expressed only in the electron density. In this chapter, we describe the details of the AIMD method with the OFDF.

Firstly, we consider the classical-dynamics of atoms on a potential energy surface $E_{tot}\left[\rho(\vec{r}),\{\vec{R}_i\}\right]$. In the AIMD method with the OFDF, the Lagrangian of the system is given by

$$L=\frac{1}{2}\mu\int d\vec{r}\left|\dot{\rho}(\vec{r})\right|^2+\frac{1}{2}\sum_i M_i\left|\dot{\vec{R}}_i\right|^2-E_{tot}\left[\rho(\vec{r}),\{\vec{R}_i\}\right]+\Lambda\left[\int\rho(\vec{r})d\vec{r}-N\right], \tag{23}$$

where μ is the fake mass of electrons, M_i is the ion mass, Λ is the Lagrange multiplier, and N is the total number of electrons in the system. The dot represents the derivative with respect to time. From the Lagrangian we can derive the equation of motion for the electron density as

$$\mu\ddot{\rho}(\vec{r})=-\frac{\delta E_{tot}}{\delta\rho(\vec{r})}+\Lambda, \tag{24}$$

and for the ion positions as

$$M_i\ddot{\vec{R}}_i=-\frac{\partial E_{tot}}{\partial\vec{R}_i}-\frac{\partial E_{II}}{\partial\vec{R}_i}, \tag{25}$$

where E_{II} is the ion-ion electrostatic energy.

If we expand the electron density into Fourier series as

$$\rho(\vec{r})=\sum_G\rho_G\,exp\left(i\vec{G}\cdot\vec{r}\right), \tag{26}$$

then Eq.(24) becomes

$$\mu\ddot{\rho}_G=-\frac{\delta E_{tot}}{\delta\rho_G}. \tag{27}$$

This equation contains no constraint terms, since the number of electrons is conserved in the first term

$$\rho_{G=0}=N/\Omega, \tag{28}$$

of the Fourier representation, where Ω is the volume of the supercell.

In the description of the DFT, the total energy of the system is expressed as

$$E_{tot}=T_P+E_{ee}+E_{xc}+E_{ext}, \tag{29}$$

where $T_P[\rho]$ is Perrot functional in Chapter Ⅱ, E_{ee} is electron-electron electrostatic energy, E_{xc} is exchange-correlation energy, and E_{ext} is electron-ion electrostatic energy. In this work, we use the E_{xc} due to Ceperley and Alder.[36]

In Fourier space the energy terms are given by

$$T_P=\Omega\sum_G\rho_G^*t_{TFvW}\left(\vec{G}\right)+\frac{\Omega}{2}\sum_G K_P\left(\vec{G}\right)\rho_G^*\rho_G, \tag{30}$$

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[35] Pearson, M., Smargiassi, E., and Madden, P.A., "*Ab initio* molecular dynamics with an orbital-free density functional", *J.Phys.Condens. Matter* vol.5, 1993, pp.3221～3240.

[36] Ceperley, D.M. and Alder, B.J., "Ground state of the Electron Gas by a stochastic method", *Phys.Rev.*Lett. vol.45, 1980, pp.566～569.

$$E_{ee} = \frac{\Omega}{2}\sum_{G\neq 0}\frac{4\pi}{G^2}\rho_G\rho_G^*, \tag{31}$$

$$E_{xc} = \Omega\sum_{G}\rho_G^*\varepsilon_{xc}\left(\vec{G}\right), \tag{32}$$

$$E_{ext} = \Omega\sum_{G\neq 0}\rho_G^* V_{ps}\left(\vec{G}\right) + N^{ion}\alpha Z_v, \tag{33}$$

with

$$V_{ps}(G) = S\left(\vec{G}\right)V_{ps}^{atom}\left(\vec{G}\right), \qquad S\left(\vec{G}\right) = \frac{1}{N^{ion}}\sum_i exp\left(-i\vec{G}\cdot\vec{R}_i\right), \tag{34}$$

$$\alpha = \frac{1}{\Omega}\int\left[V_{ps}^{atom}\left(\vec{r}\right) + \frac{Z_v}{r}\right]d\vec{r}, \tag{35}$$

where $t_{TFvW}\left(\vec{G}\right)$ is the Fourier coefficients of the TFvW energy density functional,

$$t_{TFvW}\left(\vec{r}\right) \equiv C_{TF}\rho\left(\vec{r}\right)^{2/3} + \frac{1}{8}\frac{\left|\nabla\rho\left(\vec{r}\right)\right|^2}{\rho\left(\vec{r}\right)^2}, \tag{36}$$

$V_{ps}^{atom}\left(\vec{r}\right)$ is the pseudo-potential for the atoms, $V_{ps}^{atom}\left(\vec{G}\right)$ is the Fourier coefficient of the $V_{ps}^{atom}\left(\vec{r}\right)$, Z_v is the number of valence electrons per atom, and $S\left(\vec{G}\right)$ is the structure factor. In this work, we use the pseudo-potential by Topp and Hoppfield.[37] Since the charge of the system is neutral, the two positive infinite terms of G=0 in the electron-electron and the ion-ion electrostatic energies are canceled with the negative infinite term of G=0 in the electron-ion electrostatic energy. Thus these infinite terms can be excluded from the expression for the energies and the second term in Eq.(33) is added in order to conserve the charge neutrality of the system.

The equation of motion for electron density is given by

$$\begin{aligned}\mu\ddot{\rho}_G &= -\frac{\delta E_{tot}}{\delta\rho_G} \\ &= -\frac{\delta T_{TFvW}}{\delta\rho_G} - K_P\left(\vec{G}\right)\rho_G - \frac{4\pi}{G^2}\rho_G - V_{xc}\left(\vec{G}\right) - V_{ps}\left(\vec{G}\right),\end{aligned} \tag{37}$$

where the first term is the Fourier coefficient of the functional derivative,

$$\frac{\delta T_{TFvW}}{\delta\rho\left(\vec{r}\right)} = \frac{5}{3}C_{TF}\rho\left(\vec{r}\right)^{2/3} + \frac{1}{8}\frac{\left|\nabla\rho\left(\vec{r}\right)\right|^2}{\rho\left(\vec{r}\right)^2} - \frac{1}{4}\frac{\nabla^2\rho\left(\vec{r}\right)}{\rho\left(\vec{r}\right)}, \tag{38}$$

and $V_{xc}\left(\vec{G}\right)$ is the Fourier coefficients of $V_{xc}\left(\vec{r}\right)$. In the simulation of the system at 0K, we use the steepest decent(SD) method.[38] And in the simulation of the system at finite temperature, we use the Verlet's leapfrog procedure.[39] In the simulation under NVT ensemble, we use

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[37] Topp, W.C. and Hopfield, J.J., "Chemically Motivated Pseudopotential for Sodium", *Phys.Rev.* B vol.7, 1973, pp. 1295～1303.

[38] Press, W.H., Teukolsky, S.A., Vetterling, W.T., and Flannery, B.P., *Numerical Recipes in Fortran*, 2nd edition, Cambridge, New York, 1992, p414.

[39] Verlet, L., "Computer "Experiments" on Classical Fluids. I. Thermodynamical Properties of Lennard-Jones Molecules" *Phys. Rev.* vol.159, 1967, pp.98～103.

Nosé-Hoover method.[40] The initial charge density in the simulation is obtained by superposition of atomic charge densities, and the velocities of the coefficients ρ_G are obtained by the backstep procedure. The fake mass μ in Eqs.(27) and (37) is independent of the reciprocal vector *G*. However, in order to efficient calculations, we use the *G*-dependent fake mass μ_G obtained by pre-conditioning.

The equation of motion for the ions is given by

$$\begin{aligned} M_i \ddot{\vec{R}}_i &= -\frac{\partial E_{tot}}{\partial \vec{R}_i} - \frac{\partial E_{II}}{\partial \vec{R}_i} \\ &= -\frac{\partial}{\partial \vec{R}_i}\int V_{ps}(\vec{r})\rho(\vec{r})d\vec{r} - \frac{\partial E_{II}}{\partial \vec{R}_i} \\ &= i\sum_G \rho_G^* V_{ps}(\vec{G}) exp\left(-i\vec{G}\cdot\vec{R}_I\right) - \frac{\partial E_{II}}{\partial \vec{R}_i} . \end{aligned} \tag{39}$$

The above equation is solved by the SD method or the Verlet's leapfrog procedure. The pressure is calculated by use of an equation proposed by Smargiassi and Madden.[41] They calculated the lattice parameter, bulk modulus, vacancy formation energy, and phonon dispersion curve in the crystalline sodium system. Their results were in agreement with the experiments. Although the time step Δt in the CP method[42] using wavefunctions is one-hundredth of the Δt in empirical molecular dynamics(EMD) method, the Δt in the present method is almost same as the Δt in the EMD method. Consequently, the real time evolution is extremely rapid.

Ⅳ. Computational Details

In order to simulate the sodium system, we use the AIMD method with the OFDF developed by Pearson et al. Verlet's leapfrog algorithm is used to solve CP type equations at finite temperatures. The simulations for the crystal system run with the time step $\Delta t = 100$ for 6,300 steps, and the simulations for the liquid system run with the time step $\Delta t = 30$ for 10,500 steps. The SD method is used to optimize the electronic system. We use a micro-canonical ensemble with constant volume $\Omega_{cell} = 15{,}070.358$ a.u., which is the equilibrium volume at melting point. The number of atoms in the supercell is 54. The temperature is kept fixed with the Nosé-Hoover thermostat. The cut-off energy is $E_{cut} = 12.0$ Ry. The number of FFT meshes is $32{,}768 (= (2^5)^3)$. The Topp-Hopfield local pseudopotential is used for the sodium atom. We use the Ceperley-Alder exchange-correlation energy functional.

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Ⅴ. Results and Discussion

Figure 2 shows the temperature dependence of the TF energy E_{TF} and the von Weizsäcker energy E_{vW}. In this chapter, the energy T_{TF} and T_{vW} are expressed by E_{TF} and E_{vW}, respectively. In Fig.2, the TF energy increases by 0.26 Ry and the von Weizsäcker energy increases by 0.45 Ry in the temperature range from 0 to 800 K. As reference, the melting temperature of sodium is 371 K. The TF energy decreases by 0.028 Ry in the temperature range from 370 to 500 K. On the other hand, the von Weizsäcker energy increases by 0.12 Ry. Thus the von Weizsäcker energy rapidly increases for the melting process. The ratios of the von Weizsäcker energy to the TFvW energy are 0.044 at 0 K, and 0.092 at 800 K. Thus the ratio of von Weizsäcker energy increases with elevating temperature.

The total increment of the von Weizsäcker energy from 0 to 800 K is about two times of that of the TF energy. To explain this difference we introduce the energy spectral analysis by Jones and Young.[43] They derived the second-order kinetic energies by considering the non-interacting electron gas perturbed by an external potential. In their expression, the energies are expanded into the series for reciprocal lattice vector *G* as

$$\overline{E}_{TF}[\rho] = E_{TF}[\overline{\rho}] + \frac{1}{6}\left(3\pi^2\right)^{\frac{2}{3}} \Omega_{cell} \overline{\rho}^{-\frac{1}{3}} \sum_{G\neq 0} \left|\rho_G\right|^2 \equiv \sum_G \overline{E}_{TF}[G], \tag{40}$$

$$\overline{E}_{vW}[\rho] = \frac{1}{8} \Omega_{cell} \overline{\rho}^{-1} \sum_{G\neq 0} \left|G\right|^2 \left|\rho_G\right|^2 \equiv \sum_{G\neq 0} \overline{E}_{vW}[G], \tag{41}$$

where the $\overline{\rho}$ is average charge density, the ρ_G is Fourier coefficient of charge density, and the functions $\overline{E}_{TF}[G]$ and $\overline{E}_{vW}[G]$ are the energy spectra of the $\overline{E}_{TF}[\rho]$ and the $\overline{E}_{vW}[\rho]$, respectively. The temperature dependence of the energies by Jones and Young is almost the same as that of the correct energies in Fig.2.

In the spectra $\overline{E}_{TF}[G]$ of crystalline state, there were high peaks at *G*=0.25 a.u. except for 0 K. The peak corresponds to the component of the wave-length as long as the edge-length of the supercell. In the liquid state, there was no high peak at *G*=0.25 a.u.. The vanishment of the peak component leads to the decrease of the TF energy from 370 to 500 K.

Figure 3 shows the difference $\overline{E}_{vW}[G] - \overline{E}_{TF}[G]$ at 500 and 800 K. The spectra have been averaged over the vectors of equal magnitude *G*. The spectra $\overline{E}_{TF}[G]$ at low *G*-vectors increase with elevating temperature. The spectra $\overline{E}_{vW}[G]$ at the high *G*-vector components increase with temperature than the spectra $\overline{E}_{TF}[G]$. It is found that the increment of the $\overline{E}_{vW}[G]$ is greater than that of the $\overline{E}_{TF}[G]$. In addition, there are two peaks in the difference of energy spectra as shown in Fig.3. The peak at *G*=0.7 a.u. increases in height with elevating temperature. The tails of the peak at *G*=1.1 a.u. also increase with elevating temperature although the peak at *G*=1.1 a.u. decreases. The peak at *G*=1.1 a.u. locates at the main peak of static structure factor. Thus the von Weizsäcker energy is sensitive to the atomic disorder. It is found that the increase of the charge density fluctuations induced by the atomic disorder increases the von Weizsäcker energy.

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[43] Jones, W., "Density functionals for conduction electrons in metals", *Phys.Lett.A* vol.34, 1971, pp.351～352; Jones, W. and Young, W.H., "Density functional theory and the von Weizsäcker method", *J.Phys.C: Solid State Phys.* vol.4, 1971, pp. 1332～1330.

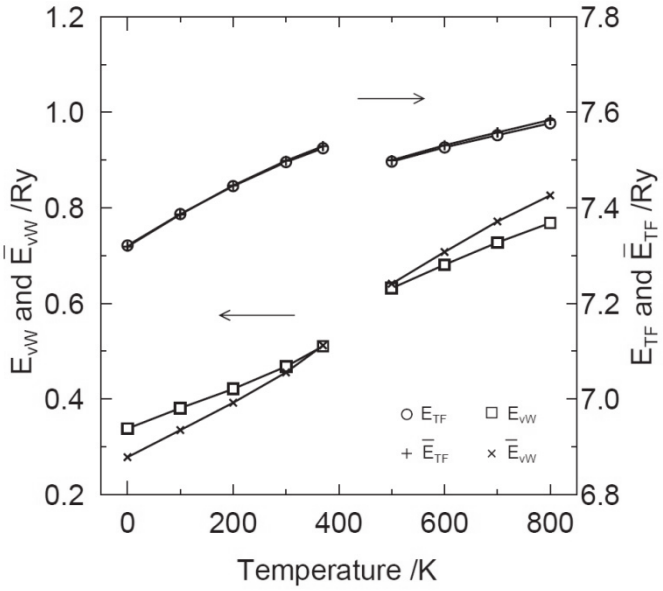

Fig.2. The TF energy E_{TF} and the von Weizsäcker energy E_{vW} as functions of temperature. The TF energy $\overline{E}_{TF}$ and the von Weizsäcker energy $\overline{E}_{vW}$ calculated with the expressions by Jones and Young are shown together.

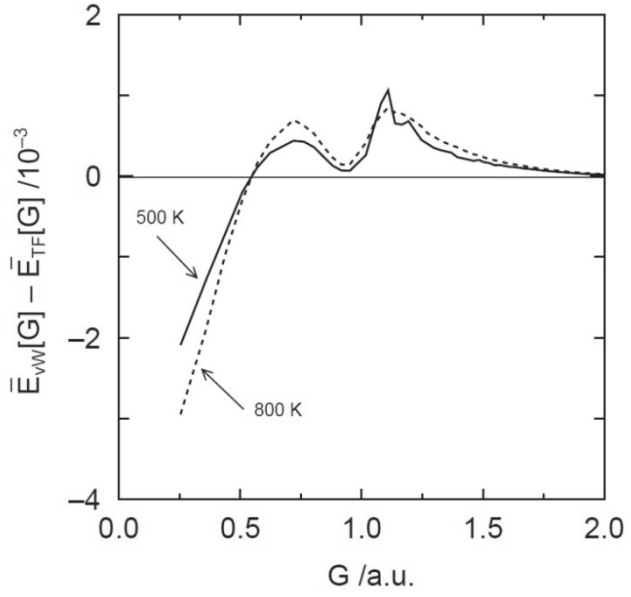

Fig.3. The temperature dependence of the difference $\overline{E}_{vW}[G]-\overline{E}_{TF}[G]$.

Ⅵ. Summary and Conclusions

We have simulated the sodium system by the AIMD method with the OFDF and then analyzed the energy spectra of the TF and von Weizsäcker energies. The earlier work based on the perturbation theory have shown that the von Weizsäcker kinetic energy term is effective for describing the electronic structure in a rapidly varying potential. However, there has been no study of the dependence of the von Weizsäcker term on atomic disorder which occurs at elevated temperature in realistic system. Accordingly we have studied the dependence with respect to the sodium system by the AIMD method with the OFDF.

As a result of the analysis, we have found the following matters. As the temperature of the system elevates from 0 to 800K, the TF energy has increased by 0.26Ry and the von Weizsäcker energy has increased by 0.45Ry. Then the ratio of von Weizsäcker energy to TFvW energy has increased from 0.044 to 0.092. That is, the weight of von Weizsäcker energy increases with elevating temperature. Also introducing the energy spectral analysis, we have found that the von Weizsäcker kinetic energy term is sensitive to the charge density fluctuations induced by the atomic disorder.

Appendix: Theory of *Homogeneous* Electron Gas

We consider *homogeneous* electron gas, of which the density is ρ_0 and the number of electrons is *N*, in the uniformly distributed positive back ground. In such a system, the HF equation is written as

$$\left[-\frac{1}{2}\nabla^2 + V_e(\vec{r}) + V_{ext}(\vec{r}) + V_x(\vec{r})\right]\phi_i(\vec{r}) = \varepsilon_i\phi_i(\vec{r}), \tag{A1}$$

where $V_e(\vec{r})$ is the electrostatic potential of electrons, $V_{ext}(\vec{r})$ is the electrostatic potential of the positive back ground, and $V_x(\vec{r})$ is the exchange potential. Although the self-energy of the electron must be extracted from the electrostatic energy, the second and third terms are canceled because the *N* and *N*-1 are almost equal for large *N*. Thus the total energy of the system per electron is written as

$$\varepsilon_{HF} = \varepsilon_{kin} + \varepsilon_x, \tag{A2}$$

where the first term is the electron kinetic energy per electron and the second term is the exchange energy per electron.

For such system, the plane wave:

$$\phi_{\vec{k}}(\vec{r}) = \frac{1}{\sqrt{\Omega}} exp\left(i\vec{k}\cdot\vec{r}\right) \tag{A3}$$

is a solution of Eq.(A1), where Ω is the volume of the system. Then the electron kinetic energy is obtained by inserting the Eq.(A3) to Eq.(A1) as

$$T = \sum_{k}^{occ.} 2\frac{\left|\vec{k}\right|^2}{2} = 2\frac{\Omega}{(2\pi)^3}\int_{k\le k_F}\frac{\left|\vec{k}\right|^2}{2}d\vec{k} = N\frac{3}{5}\frac{k_F^2}{2}, \tag{A4}$$

where k_F is the Fermi wave vector defined by

$$k_F \equiv \left(3\pi^2 N/\Omega\right)^{1/3} = \left(3\pi^2\rho_0\right)^{1/3}. \tag{A5}$$

Thus the electron kinetic energy per electron is obtained as

$$\varepsilon_{kin} = \frac{3}{10}k_F^2 = \frac{3}{10}\left(3\pi^2\right)^{2/3}\rho_0^{2/3} = \frac{3}{5}\left(\frac{9}{4\pi}\right)^{2/3}\frac{1}{r_s^2} \cong \frac{2.21}{r_s^2}(Ry), \tag{A6}$$

where r_s is the density parameter given by

$$(4\pi/3)r_s^3 = \rho_0^{-1}\,. \tag{A7}$$

The exchange energy per electron is obtained as follows. In terms of the many-electron wave function $\Psi(\vec{r}_1,\cdots,\vec{r}_N)$, the pair correlation function $\Gamma(\vec{r}_1,\vec{r}_2)$ is defined by

$$\Gamma(\vec{r}_1,\vec{r}_2) \equiv \int\cdots\int \Psi^*(\vec{r}_1,\cdots,\vec{r}_N)\Psi(\vec{r}_1,\cdots,\vec{r}_N)d\vec{r}_3 d\vec{r}_4\cdots d\vec{r}_N\,, \tag{A8}$$

apart from a normalization factor. If we approximate the $\Psi(\vec{r}_1,\cdots,\vec{r}_N)$ with a single Slater determinant, then the $\Gamma(\vec{r}_1,\vec{r}_2)$ is written as

$$\Gamma(\vec{r}_1,\vec{r}_2) = \rho(\vec{r}_1)\rho(\vec{r}_2) - \frac{1}{2}\{\rho(\vec{r}_1,\vec{r}_2)\}^2\,, \tag{A9}$$

where $\rho(\vec{r}_1,\vec{r}_2)$ is the first-order density matrix which is defined by

$$\begin{aligned}\rho(\vec{r}_1,\vec{r}_1') &\equiv \int\cdots\int \Psi^*(\vec{r}_1,\cdots,\vec{r}_N)\Psi(\vec{r}_1',\cdots,\vec{r}_N)d\vec{r}_2 d\vec{r}_3\cdots d\vec{r}_N \\ &= \sum_i^{occ.} \phi_i^*(\vec{r})\phi_i(\vec{r}')\end{aligned} \tag{A10}$$

where $\phi_i(\vec{r})$ is an orbital which builds up the single Slater determinant. Furthermore, if the $\phi_i(\vec{r})$ is replaced by the plane wave, then the $\rho(\vec{r}_1,\vec{r}_2)$ becomes

$$\rho(\vec{r},\vec{r}') = \frac{k_F^3}{2\pi^2}\frac{j_1\left(k_F|\vec{r}-\vec{r}'|\right)}{k_F|\vec{r}-\vec{r}'|}\,, \tag{A11}$$

where $j_1(r)$ is spherical Bessel function of the first kind of order 1.

The first term in Eq.(A9) becomes ρ_0^2, and substituting Eq.(A11) for second term in Eq.(A9) we obtain the pair correlation function

$$\Gamma(\vec{r},\vec{r}') = \rho_0^2 - \frac{9}{2}\rho_0^2\left\{\frac{j_1\left(k_F|\vec{r}-\vec{r}'|\right)}{k_F|\vec{r}-\vec{r}'|}\right\}^2\,. \tag{A12}$$

We express a pair distribution function of N-1 electrons for an electron (spin-up) at origin as

$$g(r) = 1 - \frac{9}{2}\left\{\frac{j_1(k_F r)}{k_F r}\right\}^2\,, \tag{A13}$$

where we normalized the function as

$$g(r) = 1/2 \quad : r \to 0 \quad \text{for electrons in spin-down state,} \tag{A14}$$

$$g(r) = 1 \quad : r \to \infty \quad \text{for electrons in both spin state.} \tag{A15}$$

Equation (A13) is a distribution function of the other N-1 electrons, constrained to the Pauli's exclusion principle, for the electron at origin. Then the electron density of the other N-1 electrons is expressed as $\rho_0 g(r)$. Figure A1 shows the distribution which is called *exchange hole* or *Fermi hole*. Since the Fermi hole density is expressed by $\rho_0\{g(r)-1\}$, the exchange energy per electron is expressed as the electrostatic potential energy. Thus we obtain

$$\varepsilon_x = \frac{1}{2}\int\frac{\rho_0\{g(r)-1\}}{r}d\vec{r} = -\frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3}\rho_0^{4/3} \cong -\frac{0.916}{r_s}(Ry)\,. \tag{A16}$$

The exchange potential V_x is given by

$$V_x = \varepsilon_x + \rho\frac{\delta\varepsilon_x}{\delta\rho} = \varepsilon_x - \frac{r_s}{3}\frac{d\varepsilon_x}{dr_x} \cong -\frac{1.22}{r_s}(Ry) \tag{A17}$$

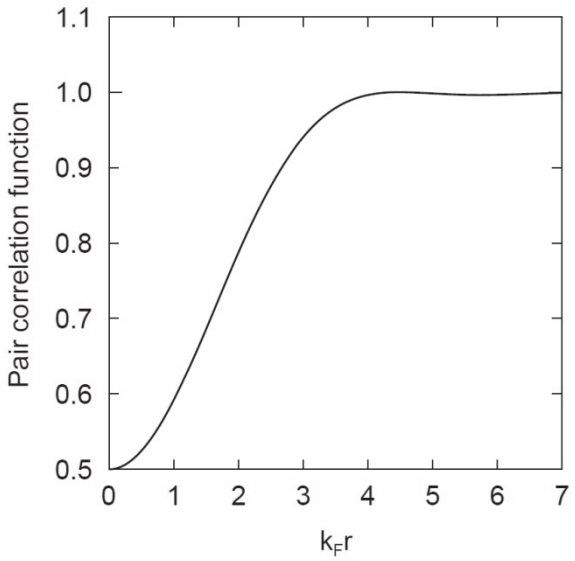

Fig.A1. Exchange hole in *homogeneous* electron gas.

The correlation energy is defined by

$$E_c \equiv E_{exact} - E_{HF}. \tag{A18}$$

However, it has been impossible to obtain this energy functional formula analytically even for the *homogeneous* electron gas system. Therefore the formula must be determined numerically. The most widely used formula for the functional is the interpolation formula by Perdew and Zunger.[44] They used the results of Green function Monte calro calculation by Ceperley and Alder.[45] The formula is given by

$$\varepsilon_c = \begin{cases} \dfrac{-0.1423}{1+1.0529\sqrt{r_s}+0.3334 r_s} & : r_s \geq 1 \\ -0.048 + 0.0311 \ln r_s - 0.0116 r_s + 0.002 r_s \ln r_s & : r_s \leq 1 \end{cases}. \tag{A19}$$

The correlation potential V_c is given by

$$V_c = \varepsilon_c + \rho \frac{\delta \varepsilon_c}{\delta \rho} = \varepsilon_c - \frac{r_s}{3} \frac{d\varepsilon_c}{dr_s}. \tag{A20}$$

Thus the exact total energy of the *homogeneous* electron gas per electron is obtained by

$$\varepsilon_{exact} = \varepsilon_{kin} + \varepsilon_x + \varepsilon_c. \tag{A21}$$

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[45] Ceperley, D.M. and Alder, B.J., "Ground state of the Electron Gas by a stochastic method", *Phys.Rev.*Lett. vol.45, 1980, pp.566～569.

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